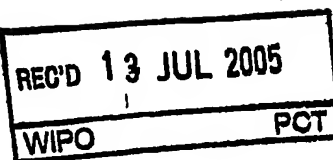


# PATENT COOPERATION TREATY

## PCT



### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>PCT/8115725</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/SG 2004/000014</b>	International filing date ( <i>day/month/year</i> ) <b>15 January 2004 (15.01.2004)</b>	Priority Date ( <i>day/month/year</i> ) <b>24 January 2003 (24.01.2003)</b>
International Patent Classification (IPC) or national classification and IPC  <b>IPC<sup>7</sup>: C02F 1/58</b>		
Applicant <b>TEOH ENG-CHYE</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examination Authority and is transmitted to the applicant according to Article 36.	
2. This REPORT consists of a total of <u>  4  </u> sheets, including this cover sheet.	
<input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).	
These annexes consist of a total of <u>  11  </u> sheets.	
3. This report contains indications relating to the following items:	
I.	<input checked="" type="checkbox"/> Basis of the opinion
II.	<input type="checkbox"/> Priority
III.	<input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV.	<input checked="" type="checkbox"/> Lack of unity of invention
V.	<input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI.	<input type="checkbox"/> Certain documents cited
VII.	<input type="checkbox"/> Certain defects in the international application
VIII.	<input type="checkbox"/> Certain observations on the international application

Date of submission of the demand  <div style="text-align: center;"><b>15.07.2004</b></div>	Date of completion of this report  
Name and mailing address of the IPEA/AT Austrian Patent Office Dresdner Straße 87 A-1200 Vienna Facsimile No. 1/53424/200	Authorized officer  <div style="text-align: center;"><b>KOLLER G.</b></div> Telephone No. 1/53424/458

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/SG 2004/000014

## I. Basis of the report

1. With regard to the elements of the international application:\*
  - ☐ the international application as originally filed
  - ☒ the description:
    - pages 12 (abstract), as originally filed
    - pages \_\_\_\_\_, filed with the demand
    - pages 1-9, filed with the letter of 3 December 2004 (03.12.2004).
  - ☒ the claims:
    - pages \_\_\_\_\_, as originally filed
    - pages \_\_\_\_\_, as amended (together with any statement) under Article 19
    - pages \_\_\_\_\_, filed with the demand
    - pages 10-11, filed with the letter of 3 December 2004 (03.12.2004).
  - ☐ the drawings:
    - pages \_\_\_\_\_, as originally filed
    - pages \_\_\_\_\_, filed with the demand
    - pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
  - ☐ the sequence listing part of the description:
    - pages \_\_\_\_\_, as originally filed
    - pages \_\_\_\_\_, filed with the demand
    - pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.  
These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:
  - ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
  - ☐ the language of publication of the international application (under Rule 48.3(b)).
  - ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
  - ☐ contained in the international application in printed form.
  - ☐ filed together with the international application in computer readable form.
  - ☐ furnished subsequently to this Authority in written form.
  - ☐ furnished subsequently to this Authority in computer readable form.
  - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
  - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.
4. ☒ The amendments have resulted in the cancellation of:
  - ☒ the description, pages 1-9.
  - ☒ the claims, Nos. 1-8.
  - ☐ the drawings, sheets/fig \_\_\_\_\_.
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as „originally filed“ and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/SG 2004/000014

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement			
Novelty (N)	Claims	1-3, 7	YES
	Claims	4-6, 8	NO
Inventive step (IS)	Claims	1-3, 7	YES
	Claims	4-6, 8	NO
Industrial applicability (IA)	Claims	1-8	YES
	Claims	----	NO

### Citations and explanations (Rule 70.7)

The following documents have been cited in the Search Report:

D1: SU 923961 A1

D2: JP 09 122690 A

D3: US 5716528 A

D4: JP 2000 135492 A

D5: JP 05 064789 A

The subject matter of claims 1-3 relates to the reaction of nitrosonium ions – generated from nitrites or nitric acid – with organic nitrogen containing compounds at elevated temperature, which is restricted to a range of from 20 to 40°C.

Referring to applicant's argumentation concerning the presence of halide ions in the liquid to be treated it is agreed, that the method according to document D1 requires the presence of halide ions. Following the applicant's argumentation the presence or absence of halides is not essential for the subject-matter of claims 1-3. Thus, the process according to the present claims 1-3 differs significantly from that of document D1 in tolerating but not needing halide ions.

The process according to document D2 relates to the removal of organic nitrogen containing compounds from industrial waste water by treatment with sodium nitrite followed by filtration, ion exchange and ultra filtration. Accordingly, document D2 is not considered to be of particular relevance concerning the subject-matter of claims 1-3.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/ SG 04/00014

## Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Box V (page 1)

Accordingly, the subject-matter of the present claims 1-3 meets the requirements of Article 33(2) and (3) PCT, that means it is new and inventive.

Documents D3 to D5 are considered for the purpose of the subject-matter of the present claims 4-8, which represent a subject-matter without any common feature linking it to claims 1-3. Both of the independent claims represent single-step processes.

The subject-matter of claim 4 relates to a method for the removal of organic and inorganic contaminants from aqueous liquids including the addition of "a peroxide" in the presence of "suitable catalysts" at "controlled pH". There is no specification of the source of peroxide, which catalyst is used or which pH-value is to be controlled.

According to document D3 organic contaminants in waste water are efficiently removed by oxidation with hydrogen peroxide in the presence of catalytic amount of ferrous ions at an acid pH.

The abstract of document D5 describes the decomposition of waste water with hydrogen peroxide and a decomposition catalyst in the presence of activated carbon.

There is no indication in the present claim 4 excluding the need of ferrous ions or an acidic pH.

Both of the documents D3 and D5 indicate the use of hydrogen peroxide as the agent for the oxidation and perform the process at an acidic pH.

Although documents D3 to D5 mention the presence of activated carbon none of said documents indicates activated carbon as the catalyst.

Consequently, the subject-matter of the present claims 4-6 and 8 is not considered to meet the requirements of Article 33(2) and (3) PCT, that means it is not new or inventive. Claim 7 meets the above mentioned requirements.

The industrial applicability is acknowledged.

03 DECEMBER 2004

**METHODS FOR THE REMOVAL OF ORGANIC NITROGEN, ORGANIC  
AND INORGANIC CONTAMINANTS FROM AN AQUEOUS LIQUID**

**FIELD OF THE INVENTION**

The present invention relates to methods for the removal of organic nitrogen, organic and inorganic contaminants from an aqueous liquid. More particularly, the present invention related to a process for the removal of organic and inorganic contaminants from wastewater and ground water.

**BACKGROUND ART**

Publicly owned treatment works (POTW) generally cannot handle industrial wastewater, which contains high levels of contaminants that are toxic, inhibitory or recalcitrant to biological treatment (e.g. pesticides, biocides, coolants and dyestuff). Industrial waste treatment plants are used to treat the high strength and low flow industrial effluent to reduce the Chemical Oxygen Demand (COD) and the Biological Oxygen Demand (BOD) through processes such as chemical oxidation prior to discharge to POTW or to watercourses.

Organic nitrogen in wastewater is usually broken up into ammonia and during the oxidation process the ammonia is oxidised to form nitrates. As a result, the presence of a high nitrogen content in effluent discharge often results in a high nitrate nutrient

AMENDED SHEET

03 DECEMBER 2004

content in treated water discharge. The biological process for nitrogen removal is slow and generally requires either a large area or large volume tank.

A nitrosonium ion forms unstable intermediates with aliphatic amines and amino compounds. This process can be used to remove organic nitrogen (such as in amines, amides and amino acids) from effluent as nitrogen gas prior to the oxidation process thereby lowering the nitrogen nutrient content of discharged water.

Reagents such as permanganate, chlorine gas, hypo-chloride, ozone, and ozone with ultraviolet light (UV), hydrogen peroxide and hydrogen peroxide with or without metallic ion catalysts, UV light or ozone have been used for chemical oxidation. Ozone has been used together with activated carbon in biological activated carbon (BAC) processes to oxidise complicated non-biodegradable organic contaminants to simpler molecules for biological treatment.

The activated carbon is normally used only as an absorbent for the organic contaminants. The activated carbon is used either after the oxidation process to remove any recalcitrant contaminants and oxidation by-products in a separate stage or to adsorb the organic contaminants through physical-chemical means from the fluid onto the solid carbon media before oxidising the contaminants.

The main disadvantage of ozone is the high cost and low efficiency of ozone generating equipment. UV activated processes require large reactor sizes to achieve sufficient contact resulting in high capital cost. The efficiency of UV treatment is very dependent on the

03 DECEMBER 2004

turbidity of the water and any other hindrances to the transmission of UV light through the water. Hydrogen peroxide with dissolved iron salts, for example Fenton's reagent, requires low pH (2-3) for oxidation and neutralisation (5.5 - 9) before the water can be disposed. Activation with metallic ions is also problematic as large amounts of bulky ferric hydroxide precipitate are formed which must be removed.

Accordingly there is a need for a process of treating aqueous liquid which may overcome some if not all the above-cited problems. Such a process is provided by the present invention.

The present invention consists of certain novel features and in combinations of parts hereinafter fully described and illustrated in the accompanying description, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the scope of the invention, or sacrificing any advantage of the present invention.

03 DECEMBER 2004

## SUMMARY OF THE INVENTION

Accordingly, the present invention provides a method for removing organic nitrogen from an aqueous liquid, said method includes the step of adding a nitrosonium ion generator into said aqueous liquid to remove nitrogen from organic based nitrogen contaminants such as amines, amides, urea and amino acids at a controlled temperature.

Also provided is a method for removing organic and inorganic contaminants from an aqueous liquid, said method includes the step of adding a peroxide in the presence of a suitable catalyst at controlled pH to oxidise and remove organic and inorganic contaminants wherein the catalyst is used as a particulate in a fixed bed reactor or moving bed reactor caused by the motion of fluid or gases, or by mechanical means through which the aqueous liquid to be treated comes in continuous contact with the catalyst in the presence of the peroxide.



03 DECEMBER 2004

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The present invention relates to methods for the removal of organic nitrogen, organic and inorganic contaminants from an aqueous liquid. More particularly, the present invention related to a process for the removal of organic and inorganic contaminants from wastewater and ground water. Hereinafter, this specification will describe the process according to the preferred embodiments of the present invention and by referring to the accompanying description. However, it is to be understood that limiting

the description to the preferred embodiments of the invention is merely to facilitate discussion of the present invention and it is envisioned that those skilled in the art may devise various modifications and equivalents without departing from the scope of the appended claims.

Nitrogen in nitrogen containing organic contaminants, such as aliphatic amines, amides, amino acids and their salts and urea may be removed by reacting contaminated water with a nitrosonium ion. The nitrosonium ion may be generated in-situ through the addition of a nitrite in acidic media to the contaminated water at room temperature or higher temperature, prior to the peroxide/carbon oxidation process described below. The removal of part or all the organic nitrogen will reduce the nitrogen content as either ammonia or nitrate nutrients in the final discharged water.

The contaminated water is oxidised with hydrogen peroxide in the presence of activated carbon, which enhances the rate of contaminant removal, by acting both as an accelerator for hydrogen peroxide oxidation and also as an absorbent for the some of the contaminants and the by-products.

03 DECEMBER 2004

The use of hydrogen peroxide solution simultaneously with activated carbon to treat water containing both organic and inorganic contaminants will simplify the process and lower the cost of the equipment required. When hydrogen peroxide is used together with activated carbon, the rate of oxidation reaction appears to be accelerated by the adsorption and concentration of contaminant molecules on the carbon surface as well as the activation and acceleration of the oxidation process at the carbon surface and in the aqueous medium. Hydrogen peroxide oxidation is effective on a diverse group of contaminants while it generates minimal secondary wastes, which are harmless (e.g. water and carbon dioxide) or biodegradable (e.g. carboxylic acids).

An overall reduction in the COD of coloured dye effluent or used machining coolant of more than 98 % is obtained by using a hydrogen peroxide and activated carbon oxidation process.

The oxidation of amines by hydrogen peroxide generates ammonia or finally nitrates in excess peroxide. The reaction rate of aliphatic amines by hydrogen peroxide is generally slow.

These two disadvantages are overcome by reacting the amines with nitrosonium ions, which are generated in-situ by metallic nitrite (e.g. sodium nitrite) in an acidic medium, to form an unstable intermediate. Slight warming of the solution accelerates the decomposition of the unstable intermediate to gaseous nitrogen and alcohol, ketone or alkene. The by-products or any excess nitrite can readily be oxidised by the hydrogen peroxide and granulated activated carbon ( $H_2O_2$  /GAC) process. Preferably the nitrogen-removal process takes place prior to the  $H_2O_2$  /GAC

03 DECEMBER 2004

oxidation process. In order to minimise the nitrogen content in the discharge water, only up to a maximum of the theoretical amount of nitrite is added. Nitrogen from amines, amides, amino acids and their salts and urea can also be removed from industrial and agricultural wastewater by this method.

The rate of colour and contaminants removal of dye contaminants from coloured dye effluent with hydrogen peroxide/granulated activated carbon ( $H_2O_2$ /GAC) process is 50 times faster than with granulated activated carbon alone and more than 200 times faster than with unactivated hydrogen peroxide alone. A similar rate of contaminant removal is also observed with the aqueous solution from used machining coolant.

When compared with a Fe catalysed hydrogen peroxide (for example Fenton's reagent) oxidation process at pH 3, the  $H_2O_2$  /GAC process takes less than half the time to remove the contaminants to the same extent as compared to the Fenton's reagent. Similar overall rate of contaminants removal (by comparing final COD measurements) as hydrogen peroxide activated carbon process is obtained when Fe(II), Fe(III), Cu(II) or Mn(II) ions together with activated carbon to accelerate the peroxide oxidation.

This indicates that there is a synergistic effect when hydrogen peroxide is used together with activated carbon in the removal of organic contaminants from wastewater. The  $H_2O_2$ /GAC process also has the advantage of operating at a milder pH and does not produce any additional metallic hydroxide slurry.

03 DECEMBER 2004

The activated carbon activator is used in various configurations, as a suspension in a batch reactor whereby it is simply stirred by the gas generated within the reactor or by a mechanical stirrer, or as particulate in a fixed or moving bed reactor through which the fluid either flow upwards or downwards for a continuous process. For a continuous process, it is also being kept in motion or fluidised through the motion of the fluid or by pressurised gas fed from the bottom of the reactor or through the motion of the bulk fluid by a mechanical stirrer.

The greatest advantages of the process are its simplicity, the ability to treat a high concentration of contaminant and the rapid treatment time. The simplicity and efficiency of the process allows a simpler and more compact plant to be built. Since it is a non-thermal, ambient pressure and aqueous process for aqueous effluent, it has a relatively lower operating cost than a thermal process. It uses readily available and inexpensive reagents. The used GAC can be regenerated and recycled. Hydrogen peroxide oxidation is effective for a diverse group of contaminants and it produces minimal secondary waste.

#### EXAMPLE A

Used machining coolant at 5% oil concentration, pH 9.3 and COD value of 35,000mg O<sub>2</sub>/l is chemically split to separate the oil from the aqueous portion. Sodium nitrite (5gm/l) is added to the aqueous portion at pH 3, COD value of 15,000 mg O<sub>2</sub>/l. The reaction temperature is 28°C or higher. Amine nitrogen is first removed from the aqueous portion. After 1-2 hour, the pH of the solution is adjusted to pH 6.5 to 9.0 and

03 DECEMBER 2004

treated with 50%  $\text{H}_2\text{O}_2$  (65gm/l) together with granular activated carbon (-12 + 30 mesh, I2 No. 1000mg/g). After about 4-12 hours, the COD drops to about 180 mg  $\text{O}_2$ /l and clear decolourised water is obtained. There is a reduction of 98.8% in the COD value during the oxidation process alone in the aqueous phase.

#### EXAMPLE B

A coffee coloured dye effluent containing 410mg/l "Dygon" No.7 dye; 10gm/l sodium chloride with a COD of 1100mg  $\text{O}_2$ /l at pH 6.5 is treated with 50%  $\text{H}_2\text{O}_2$  (4.5gm/l) together with granular activated carbon (-12 + 30 mesh, I2 No. 1000mg/g) after adjusting the pH to 8.0. After 1-2 hours, the reduction in colour is >99% and the final COD value is <10mg  $\text{O}_2$ /l, giving a COD reduction of > 99%. The final pH of the clear, decolourised solution is 7.5.

While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

03 DECEMBER 2004

## CLAIMS

1. A method for removing organic nitrogen from an aqueous liquid, said method includes the step of adding a nitrosonium ion generator into said aqueous liquid to remove nitrogen from organic based nitrogen contaminant such as amines, amides, ureas and amino acids at a controlled temperature.
2. A method as claimed in claim 1, wherein the nitrosonium ion is a nitrous acid or a nitrite in acidic media.
3. A method as claimed in claim 1, wherein the temperature is between 0°C to 100°C, preferably between 20°C to 40°C.
4. A method for removing organic and inorganic contaminants from an aqueous liquid, said method includes the step of adding a peroxide in the presence of suitable catalyst(s) at controlled pH to oxidise and remove organic and inorganic contaminants wherein the catalyst(s) is used as a particulate in a fixed bed reactor or moving bed reactor caused by the motion of fluid or gases, or by mechanical means through which the aqueous liquid to be treated comes in continuous contact with the catalyst in the presence of the peroxide.
5. A method as claimed in claim 4, wherein the addition of hydrogen peroxide can be before or together with the catalyst.

U 3 DECEMBER 2004

11

6. A method as claimed in claim 4, wherein the peroxide is hydrogen peroxide.
7. A method as claimed in claim 4, wherein the catalyst is activated carbon.
8. A method as claimed in claim 4, wherein the pH range is selected from 2 to 12.

AMENDED SHEET